

Improved Transparent Conducting Oxides for Photovoltaics

Final Research Report
1 May 1999–31 December 2002

T.O. Mason, R.P.H. Chang, T.J. Marks, and
K.R. Poeppelmeier
Northwestern University
Evanston, Illinois



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

Improved Transparent Conducting Oxides for Photovoltaics

Final Research Report
1 May 1999–31 December 2002

T.O. Mason, R.P.H. Chang, T.J. Marks, and
K.R. Poeppelmeier
Northwestern University
Evanston, Illinois

NREL Technical Monitor: R. Matson

Prepared under Subcontract No. AAD-9-18668-05



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

This publication was reproduced from the best available copy
Submitted by the subcontractor and received no editorial review at NREL

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Table of Contents

Objectives	1
Approach.....	1
Executive Summary of Research Highlights	1
Bulk TCO Research Results	2
Thin Film TCO Research Results	5
Major Scientific Findings	10
Publications.....	10

List of Figures

Figure 1. 1175°C (air) subsolidus phase diagram for the Cd-In-Sn-oxide system	3
Figure 2. Molecular structures of the metal-organic film growth precursors. (a) Bis(hexafluoroacetylacetonato)(tetramethylethylenediamine)cadmium(II), Cd(hfa) ₂ (TMEDA). (b) Tris(dipivaloylmethanato)indium(III), In(dpm) ₃	6
Figure 3. Optical properties as a function of In doping content for Cd _{1-x} In _x O films. (a) Transmittance as a function of incident wavelength. (b) Derivation of the apparent band gaps.....	7
Figure 4. Relationship between Sn doping level and electrical properties of CdO films.....	9

List of Tables

Table I. Charge transport characteristics of Cd _{1-x} In _x O films	7
Table II. The ω -rocking curve and bandgap energy data for CdO thin films with different Sn doping levels	8

Research Topic: Improved Transparent Conducting Oxides for Photovoltaics

Objectives: This subcontract focused on next-generation transparent conducting oxides (TCOs) for improved PV performance. More specifically, there were two research foci—1) improved Sn-based, n-type TCOs aimed at enhanced CdTe PV cell performance, and 2) novel Cu-based, p-type TCOs applicable to a variety of PV designs. The objective of the research under this subcontract was to identify, explore, evaluate, and develop future generations of photovoltaic technologies that can meet the long term goal of producing low-cost electricity from sunlight.

Approach: A combination of bulk and thin film studies was employed to discover, synthesize, characterize, and optimize novel TCO phases in promising Cd/Sn-based and Cu-based systems. The Cd/Sn-based materials have potential as n-type TCOs for existing photovoltaic cells, whereas the Cu-based materials are p-type and represent enabling technology for future PV designs.

Executive Summary of Research Highlights:

- Novel n-type TCO solid solution phases have been discovered and characterized. In the Cd-In-Sn-oxide ternary the following have been found: a continuous spinel solid solution between CdIn_2O_4 and Cd_2SnO_4 (near-cadmium stannate compositions are metastable), a co-doped bixbyite solid solution ($\text{In}_{2-2x}\text{Cd}_x\text{Sn}_x\text{O}_3$ out to $x = 0.34$), a co-doped orthorhombic perovskite solid solution ($\text{Cd}_{1-x}\text{Sn}_{1-x}\text{In}_{2x}\text{O}_3$ out to $x = 0.045$). In addition, extended metastable solid solutions of In or Sn in CdO have been seen in thin films, out to $x \sim 0.11$ in $\text{Cd}_{1-x}\text{In}_x\text{O}$ (by metal-organic chemical vapor deposition) and $x \sim 0.12$ in $\text{Cd}_{1-x}\text{Sn}_x\text{O}$ (by pulsed laser deposition).
- Novel p-type TCO solid solution compositions have been discovered and characterized. By low temperature/pressure hydrothermal synthesis (HTS—see below), the $\text{CuAlO}_2\text{-CuGaO}_3$ solid solution was successfully synthesized. This solid solution cannot be synthesized by conventional methods.
- The equilibrium solid state phase relations have been established (at 1175°C in air) for the $\text{CdO-In}_2\text{O}_3\text{-SnO}_2$ phase diagram. This diagram is a useful guide for TCO processing and doping (see below) in the system.
- A comprehensive point defect model has been developed for the various phases in the Cd-In-Sn-oxide system. This is an important guide for doping and optimization of TCO properties in the system and analogous TCO materials.
- It was shown that the co-doped bixbyite and spinel phases in the $\text{CdO-In}_2\text{O}_3\text{-SnO}_2$ system are “self-doped” by virtue of an inherent cation off-stoichiometry. As such, these materials do not require (or benefit as significantly) from a reductive annealing step during their synthesis.
- A novel low temperature/low pressure hydrothermal synthesis (HTS) method has been developed for Cu-based and Ag-based p-type TCO materials that cannot be readily synthesized by conventional methods.
- A powder-solution-conductivity apparatus has been developed for measuring the electrical conductivity of loose ceramic powders, with immediate application to novel HTS-synthesized p-type TCO powders. The method has broad applicability to

electroceramic powders, which cannot be consolidated/densified without loss of advantageous properties imparted by low temperature synthesis routes.

- Novel Sn and Cd precursors with superior properties (stability, volatility, reactivity) were developed for metal-organic chemical vapor deposition (MOCVD) of Sn- and Cd-based TCOs.
- Homogeneously doped $\text{Cd}_{1-x}\text{In}_x\text{O}$ films were grown by MOCVD on glass substrates with conductivities as high as 17,000 S/cm and mobilities of $70 \text{ cm}^2/\text{Vs}$.
- Epitaxial films of $\text{Cd}_{1-x}\text{Sn}_x\text{O}$ were grown on $\text{MgO}(111)$ substrates with conductivities as high as 42,000 S/cm and mobilities reaching $600 \text{ cm}^2/\text{Vs}$.
- *Ab initio* electronic structure calculations on doped CdO showed small conduction electron effective masses and a large upward shift of the band gap with donor doping.
- A comprehensive study of the CdIn_2O_4 - Cd_2SnO_4 spinel system, in bulk vs. thin film form, was able to correlate changes in the electronic/optical structure with variations in cation composition and the distribution of cations between tetrahedral and octahedral sites.
- High temperature electrical property measurements on bulk CuAlO_2 specimens confirmed low (and thermally activated) hole mobilities, consistent with *ab initio* electronic structure calculations.

Bulk TCO Research Results

A thorough investigation was made of the CdO - In_2O_3 - SnO_2 phase diagram at 1175°C in air by conventional solid state reaction methods. In addition to the end-member phases, each of which are excellent TCOs if properly doped, three additional ternary solid solution ranges were identified and characterized for TCO behavior. The end member spinels, CdIn_2O_4 and Cd_2SnO_4 , were known before our research commenced, however we have been able to confirm the existence of an extended solid solution over the range $0 \leq x \leq 0.75$ in the system $(1-x)\text{CdIn}_2\text{O}_4 \cdot x\text{Cd}_2\text{SnO}_4$ in bulk materials and over the entire range $0 \leq x \leq 1.0$ in thin film materials. In addition, bixbyite In_2O_3 can be extensively co-doped by CdO and SnO_2 out to $x=0.34$ in $\text{In}_{2-2x}\text{Cd}_x\text{Sn}_x\text{O}_3$. Both of these systems have bulk TCO properties comparable to those of ITO. More importantly, their properties can be chemically tailored somewhat by varying the overall composition. An additional TCO solid solution was discovered in the previously known orthorhombic perovskite, $\text{Cd}_{1-x}\text{Sn}_{1-x}\text{In}_2\text{O}_3$, out to $x=0.045$. The best bulk conductivity achieved in this phase was a factor of 4-5 smaller than that of bulk ITO.

The 1175°C (air) subsolidus phase diagram for the CdO - In_2O_3 - SnO_2 system is shown in Fig. 1. Note that the In_2O_3 end-member is shown as $\text{InO}_{1.5}$, so that composition corresponds to cation ratio in the various phases. We detected very little solid solubility of In or of Sn in CdO (in contrast to the thin film work, see below) or alternately of Cd or of In in SnO_2 . Similarly, there is very little solubility of Cd in In_2O_3 , but a measurable range of Sn solubility in In_2O_3 (i.e., "ITO"). The dashed lines in Fig. 1 indicate two-

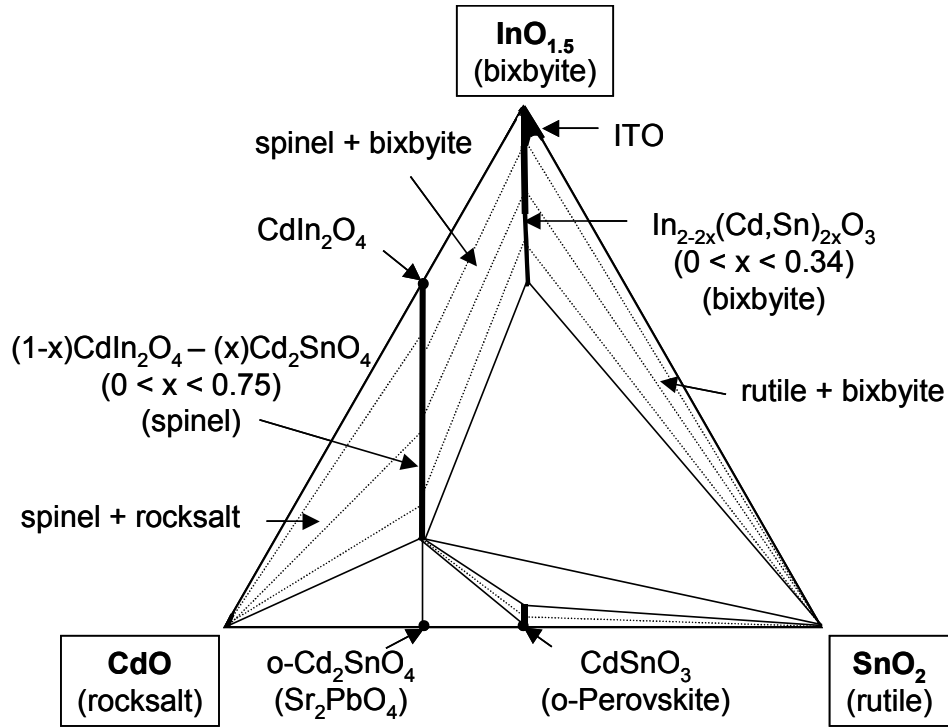


Fig. 1. 1175°C (air) subsolidus phase diagram for the Cd-In-Sn-oxide system.

phase equilibria, and the tie-triangles indicate three-phase equilibrium. This diagram is a very important tool for interpreting compatible phases and reactions in the system, and is helpful for guiding thin film studies. Furthermore, it allows important deductions to be made about the point defect mechanisms underlying carrier-doping of the TCO phases.

It would appear that hole-doping of all phases in the CdO-In₂O₃-SnO₂ system is not possible under any conditions (stable or metastable) investigated to date. This explains the solubility of higher valence (donor) cations occurs in the end members (e.g., In-doped CdO, Sn-doped CdO, and Sn-doped In₂O₃) whereas the solubility of lower valence (acceptor) cations in the end members is negligibly small (e.g., Cd-doped In₂O₃, Cd-doped SnO₂, and In-doped SnO₂).

It is also apparent that the solid solubilities represented as vertical lines in Fig. 1 must be slightly offset from perfect stoichiometry in the direction of donor-doping. This follows from the argument that the vertical lines represent isovalent doping, e.g., $\text{In}^{3+}_{2-2x}\text{Cd}^{2+}_x\text{Sn}^{4+}_x\text{O}_3$ (or two 3+ species being replaced by one 2+ species and one 4+ species) such that the concentration of donors is precisely balanced by the concentration of acceptors. Instead, we find significant electron populations in the co-doped phases. Furthermore, these phases prove to be relatively insensitive to the state of reduction, i.e., a reduction anneal does not significantly enhance the carrier populations. Our interpretation is that the vertical lines in Fig. 1 are actually shifted to the right from nominal stoichiometry such that there is an inherent donor-to-acceptor excess, leading to high electron populations. As such, these phases are “self-doped” TCOs, which do not require a reduction anneal to activate carriers, as is common with ITO and other commercial TCOs.

A systematic study was made of the cation distribution and physical properties of both bulk and thin film CdIn_2O_4 - Cd_2SnO_4 by a wide range of techniques—Rietveld analysis of X-ray diffraction and neutron diffraction data, Mössbauer spectroscopy, electrical and optical measurements. A significant portion of this work was carried out by a Northwestern graduate student during a 4-month internship at NREL. It was demonstrated that the fundamental optical gap could be tailored (by overall composition and/or thermal history, which alters the cation distribution between tetrahedral and octahedral sublattices) independent of the effective band gap (which could be altered by the carrier content). Thin films were deposited by sputter deposition from nominal composition spinel targets with electrical and optical properties comparable to those of ITO.

A theme common to much of our TCO work is that metastability can play an important factor in the synthesis of TCO materials with enhanced solubilities and improved performance. For example, the abovementioned Cd-In-Sn-oxide spinel phase is only stable in bulk form over the composition range $0 \leq x \leq 0.75$ in $(1-x)\text{CdIn}_2\text{O}_4 \cdot x\text{Cd}_2\text{SnO}_4$. In contrast, we (and others) can routinely deposit thin films over the entire composition range $0 \leq x \leq 1.0$, i.e., CdIn_2O_4 - Cd_2SnO_4 . Our interpretation is that thin film synthesis occurs at temperatures much lower than for solid state reaction, leading to metastable incorporation of higher solubilities. This was also confirmed in our thin film studies of In-doped CdO and Sn-doped CdO (see below). We also obtained enhanced solubilities in our low temperature/low pressure hydrothermal (HTS) apparatus, which we now discuss.

Much of our recent bulk synthesis effort has been devoted to the development of p-type Cu-based TCOs having the delafossite structure. Shannon (1971) demonstrated that the delafossite, CuAlO_2 , would precipitate under pressure from an alkaline solution, but the yields were low, presumably because of the low solubility of Cu^{+1} . We followed Shannon's lead and borrowed the idea from biology that in cells Cu^{+1} exists at much higher levels if there are reducing conditions. Combining the CuO/Al couple with the $\text{Cu}_2\text{O}/\text{Al}_2\text{O}_3$ couple and using the small elevated pressure in our hydrothermal unit (only 215°C) we have successfully achieved 100% yields of phase-pure CuAlO_2 . This is a significant breakthrough, since the defect populations (i.e., oxygen excess) were found to be significantly higher for hydrothermally synthesized (HS) powders than for solid state synthesis (SSS) produced powders. Furthermore, the powders are black, indicative of over-doping. Since our success with CuAlO_2 we have also synthesized AgGaO_2 and AgInO_2 by HTS. We have an ongoing interest in examining the influence of the HS route and post-annealing stages on the TCO properties (conductivity, optical transparency).

As alluded to above, we have also achieved HTS of the metastable CuAlO_2 - CuGaO_2 solid solution. What is significant about this is that, although the end members can be synthesized by standard solid state routes, the solid solution can only be made to date by hydrothermal synthesis. We have an ongoing interest in characterizing this solid solution along with other Cu-based and Ag-based delafossites for defect structure, optical and electrical properties, including the application of the powder-composite-conductivity apparatus now to be discussed.

A major recent breakthrough has been the development of a procedure to measure the electrical conductivity of loose ceramic powders without recourse to high temperature

consolidation/sintering, which would alter the enhanced properties imparted by low temperature synthesis routes. Our newly developed “powder-composite-conductivity” (PSC) apparatus involves the use of impedance spectroscopy to characterize the frequency response of a “composite” or suspension of powder to be measured in an aqueous (or other) electrolyte of known but variable conductivity. We have developed an equivalent circuit model that allows us to extract the conductivity of the powder under study. The procedure was successfully tested on TCO materials of known conductivities, including CuAlO₂ and Y-doped ITO.

We have also carried out high temperature electrical property studies on sintered bars of polycrystalline CuAlO₂. The high thermopower values obtained (>400 $\mu\text{V/K}$), regardless of attempts at doping, suggest that CuAlO₂ is highly stoichiometric and not amenable to aliovalent cation substitutions. The more telling aspect is that the mobility is activated (~ 0.14 eV activation energy) as evidenced by an activated conductivity and temperature-independent thermopower. The correspondingly low mobilities ($< 0.1 \text{ cm}^2/\text{V}\cdot\text{s}$) combined with the difficulty in doping (i.e., low hole concentrations) account for the disappointingly small conductivities routinely reported for this material. Ab initio band structure calculations in collaboration with Professor Freeman in the Dept. of Physics confirm the existence of a relatively flat valence band corresponding to large effective masses and low mobilities.

Thin Film TCO Research Results

Whereas the principal applications of TCOs are in thin film form, a fundamental understanding of growth process-microstructure-charge transport-transparency relationships is crucial to designing new and improved materials. As pointed out above, while bulk phase diagrams and crystal structures are essential foundations, they may not always reflect the rich range of metastable phases and solid solutions possible in thin films. There is a fascinating interplay between bulk and thin film phenomena which motivates a closely interfaced film growth and characterization effort by two complementary techniques: metal-organic chemical vapor deposition (MOCVD) and pulsed laser deposition (PLD). The former process offers the attraction of *in situ* growth under a variety of atmospheres, amenability to large-area coverage with high throughput, conformal coverage of complex shapes, ready control of growth chemistry. Both PLD and MOCVD have the possibility of creating metastable structures, plus the growth of multilayers. PLD is particularly convenient for growth of films and multilayers of almost any composition for rapid exploratory scouting.

A key requirement for viable MOCVD of TCOs is the availability of high-purity, thermally stable, volatile, and preferably low-melting metalorganic precursors having appropriate reactivity patterns to achieve efficient transport of the respective metal sources for clean film growth. Building on our past success in MOCVD of oxides, known and new families of multidendate ligands that saturate the metal coordination sphere have been studied and implemented in precursor synthesis and MOCVD growth of TCO films.

In particular, we have developed the first volatile, thermally stable, and easily handled MOCVD precursor for cadmium, Cd(hfa)₂(TMEDA) (hfa = hexafluoroacetylacetonate; TMEDA = tetramethylethylenediamine), shown in Fig. 2a.

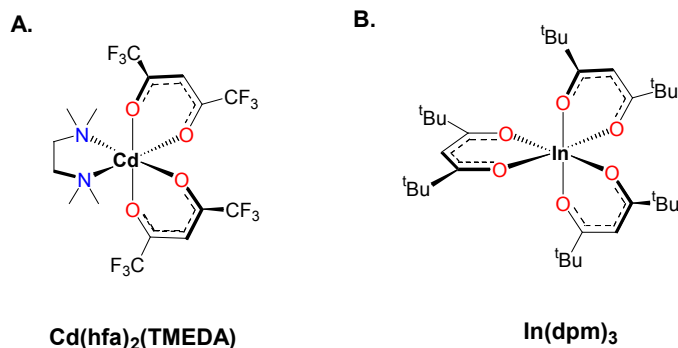


Fig. 2. Molecular structures of the metal-organic film growth precursors. (a) Bis(hexafluoroacetylacetonato)(tetramethylethylenediamine)cadmium(II), Cd(hfa)₂(TMEDA). (b) Tris(dipivaloylmethanato)indium(III), In(dpm)₃.

This was used in combination with In(dpm)₃ (dpm = dipivaloylmethanate), shown in Fig. 2b, for MOCVD of Cd-In-O films, as will now be described.

A series of Cd_{1-x}In_xO films were grown on clean float glass substrates in a low-pressure MOCVD reactor (2 Torr, 360°C substrate temperature, Ar carrier gas, H₂O-saturated O₂ reactant gas) at a growth rate of ~ 2.5 mm/min. The resulting compositions were established by inductively coupled plasma spectrometry. X-ray diffraction measurements showed the films with x ≤ 0.11 to be phase-pure, crystalline, and highly [100] textured, with features assignable to a cubic CdO-type (NaCl) crystal structure. The lattice parameters decrease monotonically with increasing x, with the reflections becoming broad for x > 0.11 and In₂O₃ peaks becoming evident. The nanostructure of the films was investigated using a cold field emission gun TEM, which confirmed the cubic structure (by electron diffraction) and pronounced [100] texture of columnar, submicron (~300 nm) grains in the x = 0.05 (most conductive) film. Microchemical sampling indicated homogenous In content throughout the film, with no evidence of grain boundary segregation or second phases being present. No other elements were detectable, with fluoride below the detection limits of ~1.2 wt%. Cross-sectional imaging indicated an atomically abrupt substrate-film interface, with no evidence of chemical reaction or solute segregation. AFM indicated the films were continuous and smooth, with rms surface roughnesses of ~10 nm over a 4 μm² area.

Table I shows the electrical properties, measured by Hall apparatus, for the Cd_{1-x}In_xO films. All films were n-type in character. The undoped CdO film had surprisingly high electrical conductivity (given its low carrier content) which was comparable to that of commercial ITO (~3000 S/cm), largely due to its excellent mobility (~150 cm²/Vs). With doping, the carrier content and electrical conductivity increased dramatically, while the mobility decreased moderately. The highest conductivity was 17,000 S/cm (at x = 0.05), with a carrier content of 1.5 × 10²¹ cm⁻³ and a mobility of 70 cm²/Vs. The fall-off in conductivity beyond x = 0.5, in spite of relatively unchanging carrier contents, was attributed to ionized impurity scattering and the concomitant decrease in electron mobility. With respect to TCO applications, the optical band gap, measured by optical absorption measurements, increased from ~2.8 eV in undoped CdO to ~3.1 eV in the x = 0.05 film, as shown in Fig. 3. The combination of the highest recorded conductivity to date (in polycrystalline films on glass) with excellent

Table I. Charge transport characteristics of $\text{Cd}_{1-x}\text{In}_x\text{O}$ films.¹

Composition x	Conductivity (S/cm)	Carrier Conc. (10^{21} cm^{-3})	Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)
0.00	3560	0.152	146
0.02	9370	0.640	91.5
0.03	15600	1.26	76.9
0.04	12300	1.27	60.5
0.05	16800	1.51	69.2
0.09	9010	1.65	34.0
0.11	6740	1.06	39.6

¹All data at 25°C.

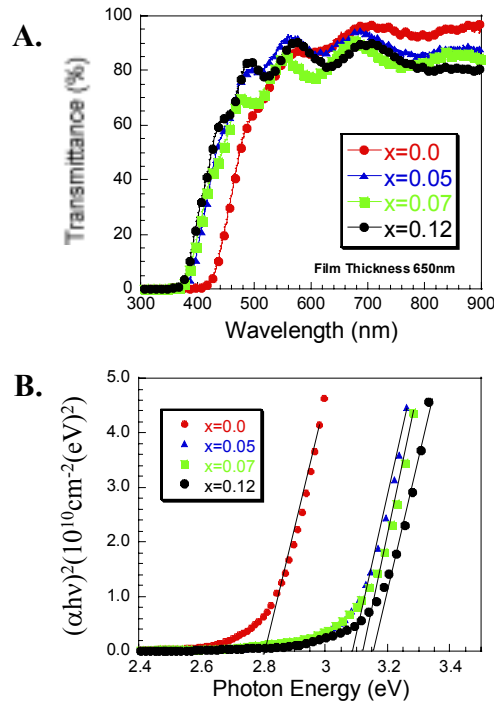


Fig. 3. Optical properties as a function of In doping content for $\text{Cd}_{1-x}\text{In}_x\text{O}$ films. (a) Transmittance as a function of incident wavelength. (b) Derivation of the apparent band gaps.

transparency throughout the visible range, makes In-doped CdO an outstanding TCO candidate.

First-principles electronic structure calculations of the $\text{Cd}_{1-x}\text{In}_x\text{O}$ system were carried out in collaboration with Professor Freeman in the Dept. of Physics at Northwestern. For the first time in a TCO, the screened exchange local density approximation method was employed. The calculated direct band gap at Γ of 2.36 eV compares well with literature reports for CdO with low carrier content. More importantly, the carrier effective masses obtained from the conduction band curvature around Γ are in the 0.24-0.26 m_e range, in contrast with the 0.3-0.42 m_e values calculated

by LDA techniques for In_2O_3 , suggesting that CdO can function as a high-mobility host lattice.

More recently we employed yet another newly developed low-melting MOCVD precursor $\text{Cd}(\text{hexafluoroacetonato})_2$ ($\text{N,N}'$ -diethyl- $\text{N,N}'$ -dimethylethylenediamine) in the MOCVD growth of high mobility cadmium-based TCO thin films. Heteroepitaxial CdO films were grown on $\text{MgO}(100)$ over the temperature range of 300 to 412°C by low pressure MOCVD. Carrier concentrations were found to decrease precipitously from 2×10^{21} to 2×10^{20} , while mobilities increase greatly from 10 to $>300 \text{ cm}^2/\text{V}\cdot\text{s}$ with increasing substrate temperature during growth. This results in conductivities $>10,000 \text{ S/cm}$ for the best of these *undoped* CdO films.

In a parallel effort, we achieved epitaxial growth of pure and Sn-doped CdO thin films on $\text{MgO}(111)$ single crystal substrates by pulsed laser deposition (PLD) over the composition range $0 \leq x \leq 0.11$. The (111) plane of CdO grew parallel to the (111) plane of the substrate. X-ray 2θ scans from 15° to 85° of both pure and Sn-doped CdO PLD films showed only the sharp peak at 33.06° corresponding to (111) CdO. As shown in Table II, the full width at half maximum increased slightly out to $x = 0.025$ in $\text{Cd}_{1-x}\text{Sn}_x\text{O}$, and thereafter increased significantly. This suggests that the epitaxial quality of the layers and the film alignment with respect to the substrate deteriorate as the Sn content increases beyond $x = 0.025$. The band gap energies determined from optical absorption measurements are also listed in Table II. These increase steadily with doping level out to $x = 0.062$ and then decrease somewhat. An SEM image of the pure CdO film was perfectly smooth, with an AFM-derived rms roughness of $\sim 3 \text{ nm}$. Upon doping with Sn to $x = 0.025$, some surface features began to appear in the SEM, and the surface roughness increased to $\sim 4 \text{ nm}$. Further increases in doping, however, resulted in far rougher surfaces by an order of magnitude, concomitant with the deterioration of the crystalline quality as pointed out above.

Table II. The ω -rocking curve and bandgap energy data for CdO thin films with different Sn doping levels.

% Sn	0.0	1.0	2.5	5.2	6.2	11.4
FWHM($^\circ$)	0.13	0.16	0.18	0.22	0.35	0.62
Bandgap(eV)	2.40	2.65	2.78	2.83	2.87	2.82

Figure 4 shows the composition dependence of electrical conductivity (σ), carrier concentration (n), and mobility (μ) in epitaxial PLD $\text{Cd}_{1-x}\text{Sn}_x\text{O}$ films. The pure CdO film has a carrier concentration of $9.2 \times 10^{19} \text{ cm}^{-3}$, corresponding to a defect density of $4.6 \times 10^{19} \text{ cm}^{-3}$. Since the lattice parameter of this film is smaller than the published ASTM bulk value, we believe the majority point defects to be oxygen vacancies. At 1% Sn doping the carrier concentration has increased by an order of magnitude, consistent with Sn acting as a doubly-charged donor. Beyond this doping level, however, the carrier content changes only slightly. This suggests that an ionic charge compensation mechanism is occurring or neutral point defect associates are being formed. Surprisingly, the mobility first increases with Sn-doping, reaching a maximum of $\sim 600 \text{ cm}^2/\text{Vs}$

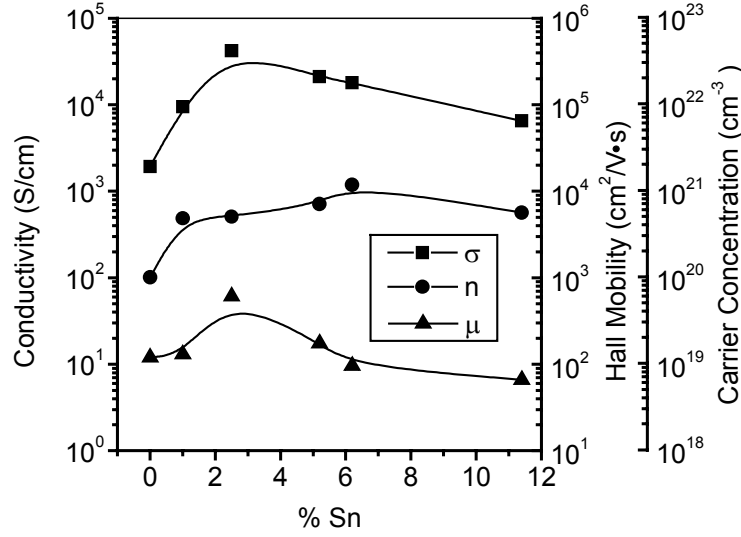


Fig. 4. Relationship between Sn doping level and electrical properties of CdO films.

at 2.5% Sn, whereafter it decreases. This behavior cannot be readily explained solely on the basis of impurity scattering. Grain boundary scattering may play an important role, with initial Sn doping resulting in a decrease of the potential barrier height at grain boundaries and correspondingly increased mobilities.

The most important observation from Fig. 4 is that electrical conductivity reaches a maximum of 42,000 S/cm in the 2.5% Sn ($x = 0.025$) film at a carrier content of $4.3 \times 10^{20} \text{ cm}^{-3}$ and a mobility of $609 \text{ cm}^2/\text{Vs}$. We believe both values, conductivity and mobility, to be records for TCO films reported to date. It must be stressed, however, that the band gaps obtained for these films (see Table II) are not quite optimal for transmission throughout the optical range. It may be possible, however, to optimize band gap by increasing the electron population (i.e., the Burstein-Moss shift), e.g., by reduction annealing and activation of otherwise neutral dopant species, as routinely performed in ITO films.

In addition to PLD of single-layer films, we have designed multiple-layer structures consisting of alternating layers of 2.5% Sn-doped CdO and 2.5% Cd-doped CdIn_2O_4 or 3% Cd-doped Cd_2SnO_4 . This appears to be a way to combine layers with high conductivity (but smaller band gap) with those of lower conductivity (but larger band gap). To date, we have been able to achieve TCO properties comparable to or better than those of ITO (e.g., 11,000 to 18,000 S/cm conductivity and optical band gaps as large as 3.03). We have an ongoing interest in the processing and properties of multiplayer TCO structures and devices.

Major Scientific Findings

In addition to finding novel phases and/or composition ranges and developing TCOs with enhanced properties, our work has led to improved understanding of the processing-structure-property relationships of TCOs:

- Metastability, whether in low temperature bulk synthesis or in thin films, can be employed to synthesize otherwise unobtainable phases, composition ranges, and doping levels for improved TCO performance
- Thin films more often than not exhibit different behavior than bulk specimens, in terms of phase stability, doping limits, and TCO properties. Quite often superior TCO behavior results.
- Simpler may be better! We have found a crude correlation between optimized electrical conductivity in a given material and its overall density of octahedrally coordinated Cd, In, and/or Sn species (in agreement with what Shannon concluded long ago!). For example, the highest density of octahedrally coordinated species occurs in the NaCl structure, as evidenced by the exceptional TCO properties of pure and donor-doped CdO.
- Self-doped TCOs can be developed, which are relatively insensitive to processing and/or reducing steps. This may prove a boon to the manufacturing of complex photovoltaic systems and devices.
- Co-doping is an important mechanism for enhancing donor and/or acceptor doping levels in TCOs and is worthy of additional study.
- The main problem to be surmounted in the Cu-based p-type TCO systems in inherently low carrier mobilities (large carrier masses). Alternate TCO-active species need to be considered.
- Exploratory synthesis and electronic structure calculations suggest that additional TCO phases and/or solid solutions remain to be discovered in “TCO space.”

Publications:

A. J. Freeman, K. R. Poeppelmeier, T. O. Mason, R. P. H. Chang, and T. J. Marks, “Chemical and thin-film strategies for new transparent conducting oxides,” *MRS Bull.*, **25** (8): 45-51 AUG (2000).

D. R. Kammler, T. O. Mason, and K. R. Poeppelmeier, “Phase Relationships, Transparency, and Conductivity in the Cadmium Indate-Cadmium Stannate System,” *Chem. Mater.*, **12** (7) 1954-1960 (2000).

A. J. Freeman, K. R. Poeppelmeier, T. O. Mason, R. P. H. Chang and T. J. Marks, “Chemical and Thin-Film Strategies for New Transparent Conducting Oxides,” *Mat. Res. Soc. Bull.*, **25** (8) 45-51 AUG (2000).

T. O. Mason, “Transparent Conducting Oxides: New Materials,” *Proc. MRS Workshop on Transparent Conducting Oxides*, Denver, CO, June 19-20, 2000 (Summary of Workshop Breakout Session).

T. J. Coutts, T. O. Mason, J. D. Perkins, and D. S. Ginley, "Transparent Conducting Oxides: Status and Opportunities in Basic Research," *Electrochem. Soc. Proc.* Vol. 99-11: Photovoltaics for the 21st Century, V. K. Kapur, R. D. McConnell, D. Carlson, G. P. Ceasar, and A. Rohatgi, eds., The Electrochemical Society, Pennington, NJ (1999) pp. 274-288.

L. N. Brewer, D. R. Kammler, T. O. Mason, and V. P. Dravid, "Combined electron diffraction/microanalysis investigation of crystallography and cation distributions in the transparent conductive oxide $\text{Cd}_{1+x}\text{In}_{2-2x}\text{Sn}_x\text{O}_4$ " *J. Appl. Phys.* **89** (2) 951-954 (2001).

D. R. Kammler, T. O. Mason, K. R. Poeppelmeier, "Bulk Phase Relations, Conductivity, and Transparency in Novel Bixbyite Transparent Conducting Oxide Solution in the Cadmium-Indium-Tin Oxide System," *J. Am. Ceram. Soc.* **84** 5 1004-1009 (2001).

M. Yan, M. Lane, C. R. Kannewurf CR and R. P. H. Chang, "Highly conductive epitaxial CdO thin films prepared by pulsed laser deposition," *Appl. Phys. Lett.*, **78** (16): 2342-2344 APR 15 (2001).

D. R. Kammler, T. O. Mason, D. L. Young, T. J. Coutts, D. Ko, K. R. Poeppelmeier, D. L. Williamson, "Comparison of Thin Film and Bulk Forms of the Transparent Conducting Oxide Solution $\text{Cd}_{1+x}\text{In}_{2-2x}\text{Sn}_x\text{O}_4$," *J. Appl. Phys.*, **90** (12) 5979-5985 DEC 15 (2001).

D. R. Kammler, T. O. Mason, D.L. Young and T. J. Coutts, "Thin Films of the Spinel $\text{Cd}_{1+x}\text{In}_{2-2x}\text{Sn}_x\text{O}_4$ Transparent Conducting Oxide Solution," *J. Appl. Phys.*, **90**, 3263-3268 (2001).

R. Asahi, J. R. Babcock, N. L. Edleman, D. R. Kammler, D. Ko, M. A. Lane, A. W. Metz, A. Wang, M. Yan, R. P. H. Chang, V. Dravid, A. J. Freeman, C. R. Kannewurf, T. J. Marks, T. O. Mason and K. R. Poeppelmeier, "New Transparent Conducting Oxides. Progress in Understanding Cadmium-Containing Bulk and Thin-Film Materials," *Electrochem. Soc. Proc.* Vol. 2001-10, R. D. McConnell and V. K. Kapur, eds., The Electrochemical Society, Pennington, NJ (2001) pp. 333-348..

A. Wang, J. R. Babcock, N. L. Edleman, A. W. Metz, M. A. Lane, R. Asahi, V. P. Dravid, C. R. Kannewurf, A. J. Freeman, T. J. Marks, "Indium-cadmium-oxide films having exceptional electrical conductivity and optical transparency: Clues for optimizing transparent conductors," *Proc. Natl. Acad. Sci. (U.S.A.)*, **98**, 7113-7116 (2001).

D. Y. Shahriari, A. Barnabe, T. O. Mason, and K. R. Poeppelmeier, "A High-Yield Hydrothermal Preparation of CuAlO_2 ," *Inorg. Chem.*, **40**, 5734-5735 (2001).

B. J. Ingram, T. O. Mason, R. Asahi, K. T. Park, and A. J. Freeman, "Electronic structure and small polaron hole transport of copper aluminate," *Phys. Rev. B*, **64**, 155114:1-7 (2001).

- J. R. Babcock, A. Wang, A. W. Metz, N. L. Edleman, M. V. Metz, M. A. Lane, C. R. Kannewurf, and T. J. Marks, "Transparent conducting CdO thin film growth using a highly volatile, thermally- and air-stable cadmium precursor," *Adv. Matls. CVD*, **7**, 239-242 (2001).
- R. Asahi, A. Wang, J. R. Babcock, N. L. Edleman, A. W. Metz, M. A. Lane, V. P. Dravid, C. R. Kannewurf, A. J. Freeman, and T. J. Marks, "First-principles calculations for understanding high conductivity and optical transparency in $\text{In}_x\text{Cd}_{1-x}\text{O}$ films," *Thin Solid Films*, **411** (1) 101-105 MAY 22 (2002).
- D. R. Kammler, B. J. Harder, N. W. Hrabe, N. M. McDonald, G. B. Gonzalez, D. A. Penake, and T. O. Mason, "Subsolidus phase relations and transparent conductors in the cadmium-indium-tin oxide system," *J. Am. Ceram. Soc.*, **85** (9) 2345-2352 SEP (2002).
- T. O. Mason, G. B. Gonzalez, D. R. Kammler, N. Mansourian-Hadavi, and B. J. Ingram, "Defect chemistry and physical properties of transparent conducting oxides in the $\text{CdO-In}_2\text{O}_3\text{-SnO}_2$ system," *Thin Solid Films*, **411** (1) 106-114 MAY 22 (2002).
- A. W. Metz, J. R. Ireland, J. Ni, K. R. Poeppelmeier, C. R. Kannewurf, and T. J. Marks, "New Low-Melting Cadmium Precursors for the Detailed Study of Texture Effects in MOCVD Derived CdO Thin-Films," *Mat. Res. Soc. Symp. Proc.* 721, J64.1-J64.6 (2002).
- J. Cui, A. Wang, N. L. Edelman, J. Ni, P. Lee, N. R. Armstrong, and T. J. Marks, "Indium-Tin Oxide Alternatives—High Work Function Transparent Conducting Oxides as Anodes for Organic Light-Emitting Diodes," *Adv. Mater.*, **13** (19) 1476 (2001).
- J. R. Babcock, A. C. Wang, A. W. Metz, N. L. Edleman, M. V. Metz, M. A. Lane, C. R. Kannewurf, and T. J. Marks, "Transparent Conducting CdO Thin Film Growth Using a Highly Volatile, Thermally and Air-Stable Cadmium Precursor," *Chem. Vapor Depos.*, **7** (6) 239 (2001).
- A. Wang, N. L. Edleman, J. R. Babcock, T. J. Marks, M. A. Lane, P. Brazis, and C. R. Kannewurf, "Metal-Organic Chemical Vapor Deposition of In-Zn-Sn-O and In-Ga-Sn-O Transparent Conducting Oxide Thin Films," *Mat. Res. Symp. Proc.*, **607**, 345-352 (2000).
- D. R. Kammler, D. D. Edwards, B. J. Ingram, T. O. Mason, G. B. Palmer, A. Ambrosini, and K. R. Poeppelmeier, "Novel Compound and Solid-Solution Transparent Conducting Oxides for Photovoltaics," in *Photovoltaics for the 21st Century*, V. K. Kapur, R. D. McConnell, D. Carlson, G. P. Ceasar, and A. Rohatgi, eds., *Electrochem. Soc. Proc.* 99-11 (1999) pp. 68-77.
- D. Y. Shahriari, A. Ambrosini, A. Barnabe, A. Wahl, and K. R. Poeppelmeier, "P-type Transparent Conductors," *CIMTEC 2002 Proceedings*, 3rd Forum on New Materials," in press.

A. Wang, N. L. Edleman, J. R. Babcock, T. J. Marks, M. A. Lane, P. R. Brazis, C. R. Kannewurf, "Growth, Microstructure, Charge Transport, and Transparency of Random Polycrystalline and Heteroepitaxial Metalorganic Chemical Vapor Deposition-Derived Gallium-Indium-Indium Oxide Thin Films, J. Mater. Res., 17, 3155-3162 (2002).

REPORT DOCUMENTATION PAGE			<i>Form Approved</i> OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE October 2003		3. REPORT TYPE AND DATES COVERED Subcontract Report 1 May 1999–31 December 2002
4. TITLE AND SUBTITLE Improved Transparent Conducting Oxides for Photovoltaics: Final Research Report, 1 May 1999–31 December 2002			5. FUNDING NUMBERS PVP32601 AAD-9-18668-05	
6. AUTHOR(S) T.O. Mason, R.P.H. Chang, T.J. Marks, and K.R. Poeppelmeier				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Northwestern University 633 Clark Street Evanston, IL 60208			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/SR-520-34825	
11. SUPPLEMENTARY NOTES NREL Technical Monitor: Richard Matson				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>): This subcontract focused on next-generation transparent conducting oxides (TCOs) for improved PV performance. More specifically, there were two research foci—1) improved Sn-based, n-type TCOs aimed at enhanced CdTe PV cell performance, and 2) novel Cu-based, p-type TCOs applicable to a variety of PV designs. The objective of the research under this subcontract was to identify, explore, evaluate, and develop future generations of photovoltaic technologies that can meet the long-term goal of producing low-cost electricity from sunlight.				
14. SUBJECT TERMS: PV; transparent conducting oxides (TCO); Sn-based; Cu-based; metal-organic chemical vapor deposition; hydrothermal synthesis (HTS); solid-state phase; powder-solution-conductivity; donor doping; thin film; electrical property measurement			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	